



Mechanistic aspects of N₂O and N₂ formation in NO reduction by NH₃ over Ag/Al₂O₃: The effect of O₂ and H₂

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ABSTRACT

A mechanistic scheme of N₂O and N₂ formation in the selective catalytic reduction of NO with NH₃ over a Ag/Al₂O₃ catalyst in the presence and absence of H₂ and O₂ was developed by applying a combination of different techniques: transient experiments with isotopic tracers in the temporal analysis of products reactor, HRTEM, in situ UV/vis and in situ FTIR spectroscopy. Based on the results of transient isotopic analysis and in situ IR experiments, it is suggested that N₂ and N₂O are formed via direct or oxygen-induced decomposition of surface NH₂NO species. These intermediates originate from NO and surface NH₂ fragments. The latter NH₂ species are formed upon stripping of hydrogen from ammonia by adsorbed oxygen species, which are produced over reduced silver species from NO, N₂O and O₂. The latter is the dominant supplier of active oxygen species. Lattice oxygen in oxidized AgO_x particles is less active than adsorbed oxygen species particularly below 623 K. The previously reported significant diminishing of N₂O production in the presence of H₂ is ascribed to hydrogen-induced generation of metallic silver sites, which are responsible for N₂O decomposition.

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1. Introduction

A negative ecological effect of nitrogen oxides (NO_x) excites enhanced efforts for the development of environmental friendly solutions for decreasing NO_x emissions. Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is considered as an efficient way for NO_x abatement from mobile diesel engines in the frame of a urea-SCR technology. Similar to selective reduction of NO_x by hydrocarbons (HC-SCR) over Ag/Al₂O₃ [1], the catalyst light-off temperature is significantly decreased (down to 473 K), when H₂ is added to NO- and NH₃-containing feeds. Such a low-temperature operation regime meets the requirements for application in mobile diesel engines. The boosting effect of H₂ on NO reduction both with hydrocarbons and ammonia may indicate that H₂ influences the same reaction steps in the SCR reaction, for example, generation of active sites or activation of NO_x. A deep understanding of the remarkable effect of H₂ on the SCR reaction over Ag/Al₂O₃ will be useful not only for further improvement of the Ag/Al₂O₃ catalysts but possibly also for the development of catalytic materials operating effectively without added H₂. Different approaches for the explanation of the role of H₂ in the SCR reaction are discussed in

the literature by now. The boosting effect of H₂ is ascribed to (i) promoting of formation of Ag_n^{δ+} clusters [1–4], essential for certain reaction pathways; (ii) the initiation of radical reactions [5,6]; and (iii) the formation of intermediate surface species like cyanides or nitrites and nitrates [5,7]. Satokawa et al. [1,2,4] have concluded on the basis of in situ UV/vis studies that H₂ facilitates the formation of moderately agglomerated Ag_n^{δ+} clusters, which are responsible for activation of hydrocarbons [3,8] or also promote dissociation of NO or O₂ [9,10]. However, in situ UV/vis spectra recorded during analysis of decane-SCR-NO_x reaction performed by Sazama et al. [5] have shown that the formation of Ag_n^{δ+} clusters containing less than 8 Ag atoms takes place even in absence of H₂. A sharp decrease in NO_x conversion rate caused by removing of hydrogen from the feed in their experiments did not lead to a respective decay in the surface coverage by Ag_n^{δ+} clusters. Co-feeding of CO instead of H₂ in the HC-SCR also resulted in the formation of Ag_n^{δ+} clusters [11]. However, no promoting effect of CO was detected. Hence, it was concluded that the activity increase of silver catalyst in selective catalytic reduction of NO_x in the presence of H₂ could not be ascribed to the facilitated formation of Ag_n^{δ+} clusters. It was assumed that hydrogen initiates radical-type reactions and increases in this way the rate of all reaction steps. According to the reaction scheme developed in Ref. [5], hydrogen dissociation over silver catalyst leads to the formation of silver hydride. The latter reacts with oxygen to hydroperoxy radicals, which in turn

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oxidize NO to NO₂ forming hydroxyl radicals. These both radical species interact with hydrocarbons yielding their oxo derivatives – formate (acrylate). An increase in surface coverage by these species during HC-SCR in the presence of gas-phase H₂ was detected by FTIR [5]. Shimizu and Satsuma [6] observed O₂[−] (super oxide) ion on the surface of Ag/Al₂O₃ after NH₃-SCR performed in the presence of H₂ at 423 K by ESR spectroscopy. These authors have suggested that these oxygen ions participate in NH_x formation from ammonia and oxidation of NO to NO₂. The latter reacts with NH_x yielding N₂ and H₂O.

Hydrogen also promotes a complex transformation of CN intermediates connected with Ag⁺ into NCO species bound to Al sites of support [5], earlier shown to be a relevant reaction step of NO_x-SCR by *in situ* FTIR studies of NO reduction with ethanol in the presence of oxygen [12]. Additionally, hydrogen reduces the concentration of surface nitrates [7], which block active sites for the SCR reaction over Ag/Al₂O₃ below 523 K.

The suggested mechanistic concepts are still controversial and in some aspects partial. For example, the reaction pathways leading to N₂O, a possible undesired side-product of this reaction, are scarcely investigated. As reported in our previous publication [10], the formation of N₂O in the SCR reaction over Ag/Al₂O₃ is significantly decreased in the presence of hydrogen. This is especially valid for low-temperature operation. From an environmental point of view, the decrease of N₂O emission is highly desirable, since N₂O contributes to global warming and ozone depletion in the upper atmosphere. Its potential to warm up the atmosphere is 310 times stronger as compared to CO₂. Besides the above environmental aspects, mechanistic understanding of reaction pathways of N₂O formation and decomposition may be helpful not only for the suppression of the N₂O emissions in NH₃-SCR over Ag-containing catalysts but also over other catalytic materials and even for other chemical processes like ammonia oxidation to nitric oxide or adipic acid production.

From the above background, the present study was aimed at elucidating of reaction pathways influencing N₂O emissions in the NH₃-SCR reaction over Ag/Al₂O₃ in the presence of O₂ and H₂. For this purpose, we investigated the origins of N₂O formation and its decomposition using isotopic tracers (¹⁵NH₃) in the temporal analysis of products (TAP-2) reactor. In order to derive insights into the redox properties of AgO_x species and into possible reactive surface intermediates, the catalysts have been characterized using HRTEM, *in situ* FTIR and *in situ* UV/vis spectroscopy. In this way, the mechanistic knowledge obtained from the transient studies can be directly related to surface intermediates and to the state of silver species under reaction conditions. This fundamental knowledge may be important for designing of catalytic materials preventing N₂O formation in the NO_x abatement from mobile diesel engines in the frame of a urea-SCR technology.

2. Experimental

2.1. Catalyst preparation

Details on the preparation procedure of Ag/Al₂O₃ catalysts have been described elsewhere [13]. Shortly, alumina hydrate powder (Disperal P2, CONDEA) was dispersed in water under intense stirring at room temperature for at least 30 min. Hereafter, an appropriate amount of 1 M AgNO₃ solution was added to the sol to achieve the desired Ag content. The immediately formed gel was filtered and dried at 393 K for 2 h. The obtained powder was compressed to pellets and subsequently crushed yielding samples with mesh sizes (ASTM) from 42 to 24 (350–710 μm). A sample used in the present study (designated as 2Ag/Al₂O₃) had an Ag loading of 1.73 wt.%. The silver content was determined by

elemental analysis (OES-ICP). The texture of the catalyst was similar to that of the alumina support. After calcination in air at 873 K for 2 h the support had a γ-Al₂O₃ phase structure with a BET surface area of 235 m² g^{−1}, a pore volume of 0.43 m³ g^{−1} and an average pore diameter of 5.2 nm.

2.2. Transient experiments

Transient studies were performed in the temporal analysis of products (TAP-2) reactor. The TAP-2 reactor system has been described in details elsewhere [14]. The catalyst (ca. 200 mg; *d_p* = 250–355 μm) was packed between two layers of quartz of the same particle size in the micro reactor made of quartz. Before transient experiments the catalyst was pre-treated at ambient pressure either in an O₂ flow (50 cm³STP/min) at 823 K for 2 h or in a flow of H₂ (H₂/Ar = 5/95, 50 cm³STP/min) at 373 K for 30 min. The pre-treated catalysts are denoted as pre-oxidized and pre-reduced, respectively. After the treatment, the catalyst was exposed to vacuum (ca. 10^{−5} Pa) and pulse experiments were carried out in the temperature range between 423 and 723 K with 100 K intervals.

Transient experiments were performed using O₂/Xe = 1/1, ¹⁵NH₃/¹⁴NO/Ne = 1/1/1 and ¹⁵NH₃/¹⁴NO/H₂/Ne = 1/1/10/1 mixtures. The pulse size was kept for all experiments in the range of 5 × 10¹⁴–9 × 10¹⁴ molecules enabling operation in the Knudsen diffusion regime and, therefore, minimizing gas-phase interactions. The following gases were applied: H₂ (5.0), Ne (4.5), Xe (4.0), O₂ (4.5), ¹⁴NO (2.5) and ¹⁵NH₃ (99.9% atoms of ¹⁵N). Isotopically labeled ammonia was purchased from ISOTEC. The following atomic mass units (AMUs) were used for mass-spectroscopic identification of different compounds: 132 (Xe), 46 (¹⁴NO₂, ¹⁵N₂O), 45 (¹⁴N¹⁵NO), 44 (¹⁴N₂O), 32 (O₂), 31 (¹⁵NO, H¹⁴NO), 30 (¹⁴N₂O, ¹⁴NO, ¹⁵N₂), 29 (¹⁴N¹⁵N), 28 (¹⁴N₂O, ¹⁴N₂), 20 (Ne), 18 (H₂O, ¹⁵NH₃), 17 (¹⁴NH₃, ¹⁵NH₃, H₂O), and 2 (H₂). For each AMU, pulses were repeated 10 times and averaged to improve the signal-to-noise ratio.

The concentration of feed components and reaction products was determined from the respective AMUs using standard fragmentation patterns and sensitivity factors, which arise from the different ionization probabilities of individual compounds. The relative sensitivities were determined as a ratio of the areas under the response signals of each compound related to the area under the response signal of inert gas. The respective areas were corrected according to the contribution of fragmentation patterns of other compounds to the measured AMU signal. The fragmentation patterns and respective sensitivities of feed components and reaction products were determined from separate calibration experiments, where a mixture of the gas and inert standard was pulsed in the reactor filled only with SiO₂ particles. It was assumed that there is no difference in the calibration values between isotopically labeled and non-labeled compounds.

2.3. UV/vis and FTIR experiments

In situ UV/vis diffuse reflectance spectra were taken on a Varian Cary 400 UV/vis spectrophotometer as described in Ref. [15]. A stainless steel reaction chamber with quartz windows was used in combination with diffuse reflectance attachment (DRA of Harrick) for measurements performed under gas feed up to 823 K. The unloaded alumina served as reference. *In situ* UV/vis spectra were measured in reflectance mode and converted into the Kubelka–Munk function, *F(R_∞)*, using implemented routine GRAMS32 (Galactic). Reduction/oxidation measurements were carried out in a quasi temperature-programmed mode as follows. Before spectra recording the catalyst was treated with an O₂/N₂ mixture (5/95, 25 cm³STP/min) at 773 K for 30 min. After cooling, a first

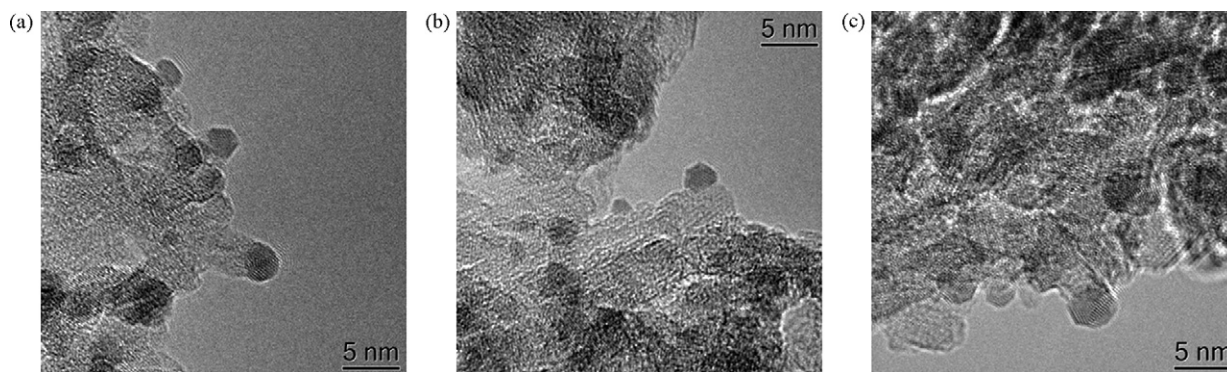


Fig. 1. TEM images of 2Ag/Al₂O₃ pre-treated under different conditions: (a) calcined at 773 K in air for 2 h, (b) reduced at 373 K by hydrogen (H₂/Ar = 5/95, 50 cm³_{STP}/min) for 2 h and (c) reduced at 473 K by hydrogen (H₂/Ar = 5/95, 50 cm³_{STP}/min) for 2 h.

spectrum was taken at room temperature. Subsequently, this O₂-containing flow was replaced by an H₂/N₂ flow (5/95, 25 cm³STP/min) and the sample was heated in steps of 20 K up to 823 K and kept at this temperature for 30 min, before returning to room temperature under flow of N₂. Oxidation was started at room temperature with the same flow that served for pre-treatment. Spectra were recorded every 50 K up to 823 K, keeping the sample at this temperature for 30 min. After completion of this cycle, a final spectrum was recorded at room temperature again.

FTIR spectra were recorded by means of a Bruker IFS 66 spectrometer using a reaction cell with CaF₂ windows, which was connected to a gas dosing–evacuation system. Adsorption experiments were performed on self-supporting wafers ($m = 50$ mg, $d = 20$ mm) of the catalyst powder.

The catalyst was either pre-oxidized in air (60 cm³STP min^{−1}) at 573 K for 1 h or pre-reduced by treating the sample with an H₂/Ar flow (5/95, 60 cm³STP min^{−1}) at 573 K for 1 h. After these pretreatment procedures, the interaction of the catalyst with the reactant mixture (100 cm³STP min^{−1}) at 423 K was monitored for 90 min. The composition of the reactant mixture was 0.04 vol.% NO/0.04 vol.% NH₃/4 vol.% O₂/1 vol.% H₂ balanced by inert gas. For one experiment a gas mixture of 0.09 vol.% NO/2 vol.% O₂ was pre-adsorbed for 30 min and, then, the catalyst was exposed to 1 vol.% H₂/Ar or 0.4 vol.% NH₃/Ar for 60 min.

2.4. HRTEM measurements

HRTEM measurements were carried out in a Philips CM200 FEG transmission electron microscope equipped with a Gatan Tridiem image filter. During storage and transportation, the samples were kept in ampoules under nitrogen atmosphere. Prior to imaging, the ampoules were opened and the samples were crushed using a mortar and pestle. The resulting powder was dispersed on a copper TEM grid covered with a holey carbon film. Images were acquired and analyzed using DigitalMicrographTM from Gatan Inc.

3. Results and discussion

The following three sections describe the results of physical and chemical characterization of 2Ag/Al₂O₃ catalytic material as well as of transient isotopic analysis. Finally, a detailed mechanistic concept of nitrogen and nitrous oxide formation in the NO–NH₃–O₂–H₂ interactions is suggested and discussed.

3.1. Catalyst morphology and redox behavior of AgO_x species

The influence of the catalyst pre-treatment on the oxidation state of silver on the catalyst surface was studied by XRD and HRTEM. XRD

measurements showed that no silver-containing crystalline phases exist in the catalyst. Nano-sized silver particles were identified on the catalyst surface by means of HRTEM analysis. Since this method does not allow detecting of Ag_n⁺ clusters on atomic level, the following discussion is related to nano-sized AgO_x species. In order to check, if the size of these species is influenced by reaction conditions, HRTEM images of oxidized and reduced samples were recorded. Fig. 1 shows TEM images of oxidized 2Ag/Al₂O₃ (calcination at 773 K in air for 2 h (Fig. 1a)), 2Ag/Al₂O₃ reduced at 373 K (Fig. 1b) and 473 K (Fig. 1c) by hydrogen (H₂/Ar = 5/95, 50 cm³STP/min) for 2 h. One can see that the average diameter of nano-sized silver particles does not depend on the type of treatment and amounts to ca. 3 nm. However, the treatment influences the oxidation state of silver. Silver exists in the form of polycrystalline silver oxide (Ag₂O) on the pre-oxidized sample. On the sample treated in hydrogen, metallic Ag nano clusters of the same size could be detected by converging beam diffraction on selected particles. This confirms that dispersion of Ag during H₂-reduction of nano-sized Ag₂O does not proceed to an extent that is recognizable by HRTEM. Clusters that undergo dispersion and agglomeration processes on the Al₂O₃ surfaces comprise 4–8 silver atoms and their formation can be deduced from EXAFS and UV/vis analysis. Thus, the existence of Ag_n^{δ+} clusters on a 2 wt.% Ag/Al₂O₃ catalyst after pre-reduction at 573 K is reported to occur [16]. Redispersal of such small clusters to Ag⁺ ions under oxidizing conditions is possible as followed from EXAFS measurements [16]. Breen et al. [17] reported that an increase in the Ag–Ag coordination is observed from EXAFS data, when the catalyst is exposed to SCR reaction conditions at 723 K using C₈H₁₈ as reductant. This effect is more pronounced if switching to reducing conditions using 8% H₂/He at the same temperature. Because no Ag–O coordination is retained under these reducing conditions, it can be concluded that all Ag_xO is completely reduced [17].

Reversible reduction/reoxidation of Ag₂O/Ag over 2Ag/Al₂O₃ was confirmed by in situ UV/vis spectroscopic analysis. In these experiments, UV/vis spectra were recorded under oxidizing (O₂/N₂ = 5/95, 25 cm³STP/min) or reducing (H₂/N₂ = 5/95, 25 cm³STP/min) conditions at different reaction temperatures. Fig. 2(a) and (b) exemplifies UV/vis spectra recorded during reduction of pre-oxidized 2Ag/Al₂O₃ by a mixture of H₂ and N₂ and during oxidation of previously reduced silver catalyst by O₂ diluted with N₂, respectively. Fig. 2(a) clearly shows an increase in the Kubelka–Munk function at ca. 420 nm. This increase becomes more pronounced with an increase in temperature. The absorption in this region reflects the existence of nano-sized Ag clusters [5,15]. Absorption within the region of 210–240 nm can be attributed to Ag⁺ isolated ions on γ-Al₂O₃ whereas a shift to higher wavelengths (260–370 nm) indicates clustering [5,15]. According to this

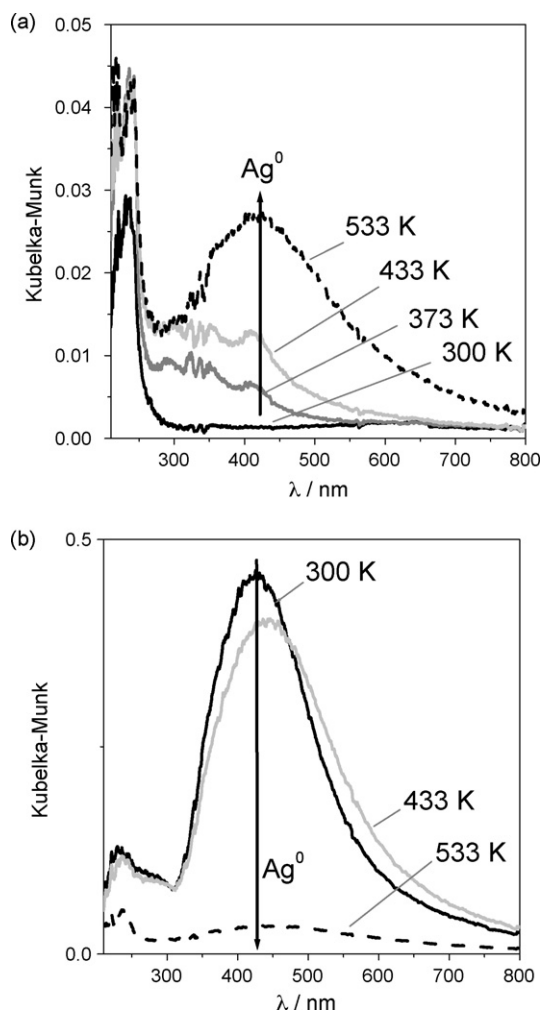


Fig. 2. In situ UV/vis spectra: (a) during reduction of oxidized 2Ag/Al₂O₃ in a H₂ flow (H₂/N₂ = 5/95, 25 cm³_{STP}/min) at different temperatures and (b) during reoxidation of reduced 2Ag/Al₂O₃ in an O₂ flow (O₂/N₂ = 5/95, 25 cm³_{STP}/min) at different temperatures.

assignment, UV/vis spectra presented in Fig. 2 confirm (i) the existence of Ag⁺ after preparation (absorption at about 240 nm) and (ii) reduction of nano-sized AgO_x species to metallic Ag ones (poorly resolved absorption between 300 and 370 nm). The reduced silver species are easily reoxidized in an O₂-containing flow even at 433 K (Fig. 2(b)). Thus it can be stated that silver species on alumina are characterized by a high degree of heterogeneity, depending on the preparation conditions, but nevertheless, two main classes are clearly distinguishable: clusters in the size range of 3–5 nm (resolved by HRTEM and UV/vis) and Ag⁺/Ag_n^{δ+} species (resolved by UV/vis). Not depending on the nature of Ag species, oxidized ones are easily reduced by H₂, while reduced ones are reoxidized by O₂.

3.2. Transient experiments over Ag/Al₂O₃

The influence of the state (oxidized and reduced) of silver particles on product formation in the ¹⁴NO–¹⁵NH₃–O₂ interactions over pre-oxidized and pre-reduced 2Ag/Al₂O₃ is shown in Fig. 3. Both, for oxidized and reduced catalyst, ¹⁴N₂, ¹⁴N¹⁵N, ¹⁴N₂O, and ¹⁴N¹⁵NO were identified as main nitrogen-containing reaction products. The presence of nitrogen atoms originating from ammonia (¹⁵NH₃) and from nitric oxide (¹⁴NO) in nitrogen (¹⁴N¹⁵N, ¹⁴N₂) and nitrous oxide (¹⁴N¹⁵NO, ¹⁴N₂O) indicates that

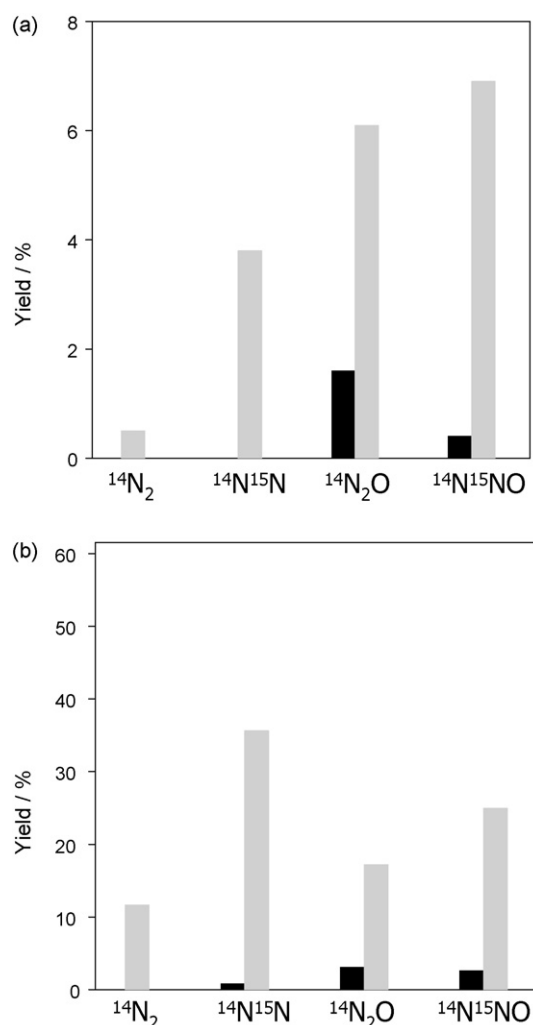


Fig. 3. Yields of reaction products upon simultaneous pulsing of O₂/Xe = 1/1 and ¹⁵NH₃/¹⁴NO/Ne = 1/1/1 mixtures at 423 K (a) and 623 K (b) over oxidized (black bars) and reduced (grey bars) 2Ag/Al₂O₃ catalyst. The ratio of O₂/¹⁴NO was ca. 10.

these products formally originate from only one type of N-containing feed molecules as well as from both types. Possible reaction pathways leading to differently labeled nitrogen and nitrous oxide are discussed in Section 3.4 taking into account the results of our in situ IR analysis (Section 3.3).

It is important to highlight that the amount of ¹⁴N₂, ¹⁴N¹⁵N, ¹⁴N₂O, and ¹⁴N¹⁵NO over reduced silver particles is considerably higher than over oxidized ones. This means that the reduced silver particles are very active in the NH₃–SCR reaction. These results agree well with earlier mentioned steady-state catalytic performance of variously loaded Ag/Al₂O₃ catalysts [9], when the NH₃–SCR reaction was performed in the presence of H₂. A detailed analysis of the role of reduced and oxidized silver species in NH₃–NO, NH₃–NO–O₂ and NH₃–NO–O₂–H₂ interactions has been previously reported by us [10]. In the present study, we particularly analyzed the role of hydrogen in N₂O and N₂ formation.

In agreement with steady-state catalytic tests [13], N₂O formation significantly decreases, when H₂ is added to an NH₃–NO–O₂ reaction mixture (Fig. 4). In order to elucidate possible mechanistic origins of this effect on N₂O production we analyzed the shapes of transient responses of N₂O and N₂ recorded during experiments with two mixtures: (i) NH₃–NO–O₂ and (ii) NH₃–NO–O₂–H₂. According to the theory of the TAP [14], the shape of transient responses contains mechanistic information on chemical

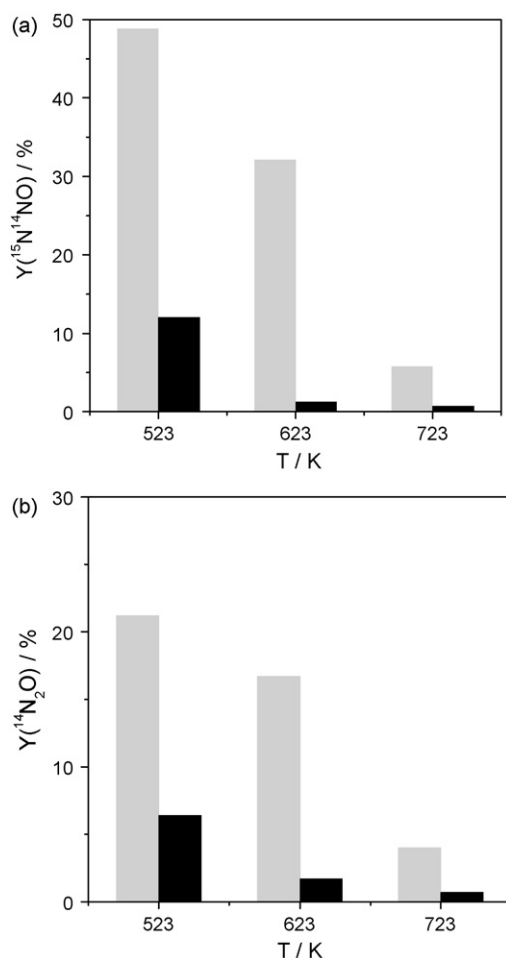


Fig. 4. Yields of $^{15}\text{N}^{14}\text{NO}$ (a) and $^{14}\text{N}_2\text{O}$ (b) upon simultaneous pulsing of $\text{O}_2/\text{Xe} = 1/1$ and $^{15}\text{NH}_3/^{14}\text{NO}/\text{Ne} = 1/1/1$ (grey bars) as well as of $\text{O}_2/\text{Xe} = 1/1$ and $^{15}\text{NH}_3/^{14}\text{NO}/\text{H}_2/\text{Ne} = 1/1/1/1$ (black bars) mixtures over $2\text{Ag}/\text{Al}_2\text{O}_3$ at different temperatures. The ratio of $\text{O}_2/^{14}\text{NO}$ was ca. 10.

processes occurring on the catalyst, like sequence of product formation. For easier comparison of the shapes of transient responses of N_2O and N_2 , they were normalized according to [14]. This procedure enables to compare the order of the appearance of gas-phase components, which differ significantly in their molecular weights.

The normalized transient responses of $^{14}\text{N}^{15}\text{NO}$, $^{14}\text{N}_2\text{O}$, $^{14}\text{N}^{15}\text{N}$ and $^{14}\text{N}_2$ recorded after simultaneous pulsing of $^{15}\text{NH}_3/^{14}\text{NO}/\text{Ne} = 1/1/1$ and $\text{O}_2/\text{Xe} = 1/1$ mixtures at 523 and 623 K are shown in Fig. 5. This figure illustrates that there are no significant differences in the shapes of N_2 ($^{14}\text{N}^{15}\text{N}$ and $^{14}\text{N}_2$) and N_2O ($^{14}\text{N}^{15}\text{NO}$ and $^{14}\text{N}_2\text{O}$) transient responses in absence of H_2 . The similar shapes of these normalized transient responses indicate that differently labeled nitrous oxide and nitrogen molecules are formed via parallel reaction pathways. This conclusion is not valid, when $^{15}\text{NH}_3$ – ^{14}NO – O_2 transient experiments are performed in the presence of hydrogen. Fig. 5 nicely shows a significant sharpening of the transient responses of $^{14}\text{N}^{15}\text{NO}$ and $^{14}\text{N}_2\text{O}$, when H_2 was pulsed together with ^{14}NO , $^{15}\text{NH}_3$ and O_2 . For example at 623 K, the widths of normalized transient responses of nitrous oxide at their half height are 0.081 and 0.023 s without and with H_2 , respectively. Moreover, the maxima (t_{max}) of normalized transient responses of nitrous oxide are shifted to shorter times as compared to those of nitrogen: t_{max} of nitrous oxide is ca. 0.018 s, while t_{max} of nitrogen is ca. 0.043 s. Such a decrease in the t_{max} of nitrous oxide but an

increase in the t_{max} of nitrogen is due to the decomposition of primarily formed nitrous oxide to nitrogen. In principle, this conclusion is valid for $^{14}\text{N}^{15}\text{NO}$, $^{14}\text{N}_2\text{O}$, $^{14}\text{N}^{15}\text{N}$ and $^{14}\text{N}_2$. However, the transient responses of nitrogen and nitrous oxide containing two types of N-atoms ($^{14}\text{N}^{15}\text{N}$ and $^{14}\text{N}^{15}\text{NO}$) are slightly stronger influenced by the presence of H_2 as compared to those containing only ^{14}N -atoms (Fig. 5). This result indirectly supports our assumption that there are two different pathways leading to product molecules with and without labeled (^{15}N) nitrogen atoms.

In order to elucidate the possible role of surface intermediates in the formation of differently labeled nitrogen and nitrous oxide, we performed FTIR analysis. The results are presented and discussed below.

3.3. Surface intermediates

As shown in our previous study [18], nitrate species were formed upon NO/O_2 adsorption over variously loaded $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts. The concentration of these adsorbed species increased in the presence of H_2 . However, these nitrate species are only characteristic for the pre-oxidized sample, whereas unstable but reactive nitrite and nitro species were formed on the pre-reduced catalyst.

The exposure of the pre-oxidized catalyst to a gas mixture of 0.04 vol.% $\text{NO}/0.04$ vol.% $\text{NH}_3/4$ vol.% O_2 led to the formation of chelating bidentate nitrate species. Fig. 6(a) illustrates time-on-stream dependence of the concentration of these species over oxidized $2\text{Ag}/\text{Al}_2\text{O}_3$ in the absence and presence of H_2 . One can see that this concentration increases with time in the absence of H_2 . When H_2 is added to an NO – NH_3 – O_2 feed the overall concentration of chelating bidentate nitrate species is significantly lower and reaches a constant value after 20 min on stream. The same effect was also found for the pre-reduced catalyst, however, the amount of nitrate species was essentially lower both during reaction with the H_2 -free and the H_2 -containing gas mixtures (Fig. 6(b)). In order to investigate whether these species react with ammonia, the pre-oxidized $2\text{Ag}/\text{Al}_2\text{O}_3$ catalyst was exposed to an NO/O_2 atmosphere followed by replacing of the oxidizing atmosphere with a reducing one. For comparison, besides 0.4 vol.% NH_3/Ar also 1 vol.% H_2/Ar was employed as reducing gas mixture. FTIR spectra recorded after different treatments are shown in Fig. 7. The broad bands around 1290 and 1560 cm^{-1} in the spectra obtained after NO/O_2 adsorption are typical for chelating bidentate nitrate species. The intensity of these bands decreases after the exposure of the catalyst to H_2 and NH_3 indicating that these nitrate species react with both, hydrogen and ammonia. The interaction with H_2 does not lead to the formation of new ad-species. However, during exposure to ammonia the formation of new type of adsorbed species is reflected by the appearance of a new band at 1394 cm^{-1} and broadened bands at 1558 and 1303 cm^{-1} , which can be attributed to adsorbed NH_2NO or HNO [19]. These adsorbed species are stable only in the presence of gas phase. Their concentration strongly decreases upon evacuation at 796 K. After evacuation, bands at 1558, 1453, 1406 and 1303 cm^{-1} remain. The intensive bands at 1558/1303 cm^{-1} indicate the presence of nitrate species. The low-intensity band at 1453 cm^{-1} results from nitrite species. The band at 1406 cm^{-1} can be assigned to NH_4^+ (additional bands in the 3300–3200 cm^{-1} region), resulting from the reaction of NH_3 with formed water. In summary, the FTIR analysis has shown that ammonia reacts in a specific way with chelating bidentate nitrate species yielding NH_2NO or HNO species.

3.4. Mechanistic aspects of the NH_3 -SCR reaction in the absence and presence of O_2

Based on the results reported here and in our previous papers [10,13], an improved mechanistic concept of the effect of oxygen

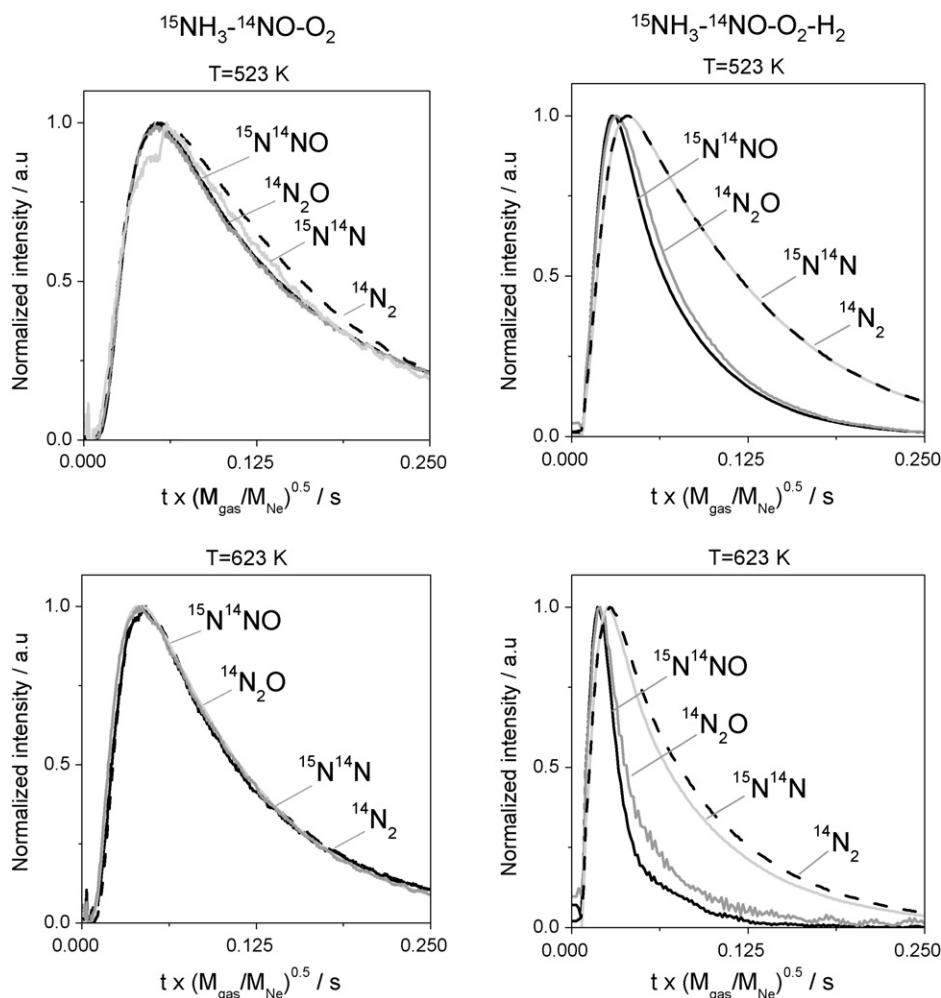


Fig. 5. Normalized transient responses of $^{14}\text{N}^{15}\text{NO}$, $^{14}\text{N}_2\text{O}$, $^{15}\text{N}^{15}\text{N}$ and $^{14}\text{N}_2$ after simultaneous pulsing of $\text{O}_2/\text{Xe} = 1/1$ and $^{15}\text{NH}_3/^{14}\text{NO}/\text{H}_2/\text{Ne} = 1/1/10/1$ mixtures over $2\text{Ag}/\text{Al}_2\text{O}_3$ at 523 and 623 K. The ratio of $\text{O}_2/^{14}\text{NO}$ was ca. 10.

and hydrogen on nitrogen and nitrous oxide formation in the $\text{NH}_3\text{-SCR}$ over $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts has been developed. A simplified scheme with the reaction network and product formation is illustrated in Fig. 8. The scheme considers reaction pathways of N_2 and N_2O formation as well as factors governing activity and selectivity of the catalyst. Black arrows represent major reaction

pathways, while the grey ones are for minor reactions. Reduced (Ag) and oxidized (AgO_x) silver species are supposed to be potential active sites in the $\text{NH}_3\text{-SCR}$ reaction. In agreement with previous studies [9,10,13], the present results proved the low activity of oxidized AgO_x species for the reaction below 723 K. The reason for the lack of activity is the inability of lattice oxygen species of AgO_x

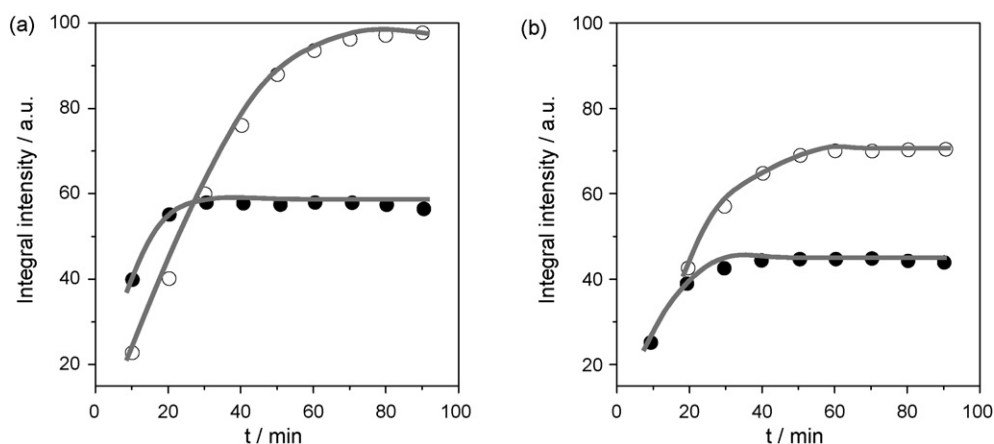


Fig. 6. Integral band intensities (1563 cm^{-1}) of nitrate species formed during interaction with 0.04 vol.% NO/0.04 vol.% $\text{NH}_3/4 \text{ vol.}\% \text{ O}_2$ (open circles) and 0.04 vol.% NO/0.04 vol.% $\text{NH}_3/4 \text{ vol.}\% \text{ O}_2/1 \text{ vol.}\% \text{ H}_2$ (full circles) on pre-oxidized (a) and pre-reduced (b) $2\text{Ag}/\text{Al}_2\text{O}_3$ catalysts at 423 K in dependence on time.

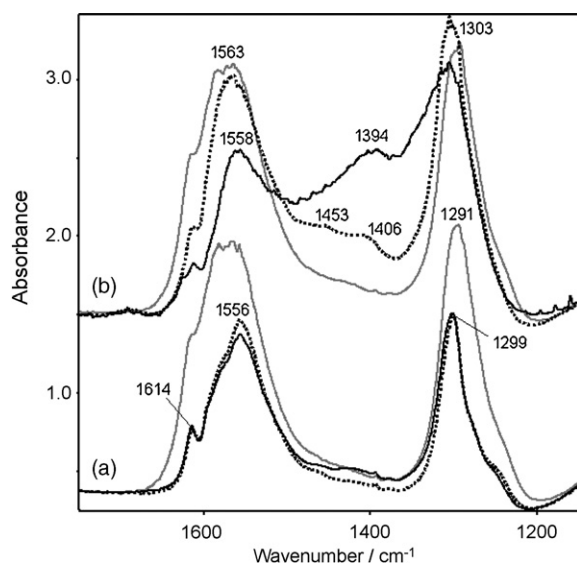


Fig. 7. FTIR spectra obtained after 30 min pre-adsorption of 0.09 vol.% NO/2 vol.% O₂ (grey lines), followed by exposure to 1 vol.% H₂/Ar (a) or 0.4 vol.% NH₃/Ar (b) for 60 min (black solid lines) and evacuation (dotted lines) at 423 K, respectively.

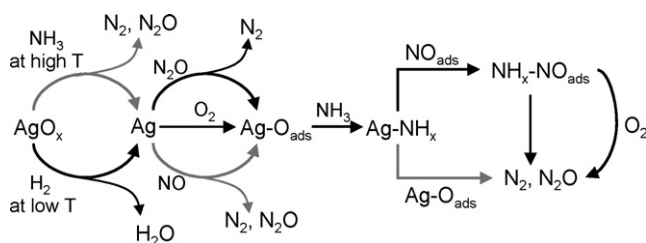


Fig. 8. Reaction network of the NH₃-SCR reaction over 2Ag/Al₂O₃.

aggregates to remove hydrogen atoms from NH₃ molecules yielding highly reactive surface NH_x fragments essential for further NO conversion. Reduced silver species formed upon reduction of oxidized AgO_x species with H₂ at temperatures above 373 K reveal, however, moderate activity towards NO reduction by NH₃ in the absence of gas-phase O₂ as it has been previously observed during pulse experiments with ¹⁵NH₃–¹⁴NO [10]. This is due to the inertness of silver in ammonia activation, i.e. in breaking N–H bonds in the ammonia molecule [20]. Stripping of hydrogen atoms from NH₃ molecules requires, therefore, participation of oxygen species. The oxygen species active in the formation of NH_x from NH₃ are denoted in the scheme as Ag–O_{ads} (Fig. 8). Concerning the nature of active oxygen species, it is well established that, depending on reaction conditions, interaction of oxygen with silver catalysts results in stabilization of various adsorbed molecular and atomic oxygen species [21–25]. Molecularly adsorbed oxygen species exist on the surface between 25 and 170 K. At higher temperatures oxygen molecules dissociate to atomically adsorbed species, which recombine and desorb above ca. 500 K. Penetration of oxygen atoms into bulk of metallic silver or formation of oxide layers is accelerated upon increasing reaction temperature and oxygen partial pressure [23,25]. Due to the variety of oxygen species, which can exist on the surface of silver catalysts in the studied temperature range, it is not possible at this stage to precisely identify the nature of oxygen species responsible for the dehydrogenation of ammonia.

Since the amount of reaction products in the NH₃–NO interactions over reduced Ag species is considerably enhanced in the presence of gas-phase O₂ [10], it is concluded that molecular

oxygen generates either more reactive surface oxygen species than NO does, and/or the concentration of oxygen species is considerably higher. Based on the experimental results on distribution of ¹⁴N and ¹⁵N in nitrogen and nitrous oxide [10], it is concluded that NO cannot be effectively decomposed over reduced Ag species with formation of N₂, N₂O and active oxygen species. This statement is supported by previous surface science studies [26,27], which reported low activity of metallic silver for NO dissociation. More typical for this metal, especially in the presence of oxygen, is the formation of NO₂ and NO₃ surface species. Depending on the reaction conditions the latter can form layers of surface nitrate [26].

Ammonia fragments (Ag–NH_x, Fig. 8) resulting from the interaction of active adsorbed oxygen species with NH₃ are essential for the formation of surface NH₂NO species identified by FTIR (Fig. 7). This surface species is a possible intermediate of gas-phase nitrogen and nitrous oxide formation. The isotopic distribution of nitrogen atoms in these products in ¹⁵NH₃–¹⁴NO–H₂–O₂ interactions indirectly supports the participation of surface NH₂NO species in the formation of gas-phase products. As shown in our previous paper [10] and in Fig. 3, ¹⁵N¹⁴N and ¹⁵N¹⁴NO are the main nitrogen-containing products of ¹⁴NO reduction by ¹⁵NH₃, i.e. these products are formed via a coupling reaction of ¹⁵NH₃ and ¹⁴NO. Moreover, ¹⁵N¹⁴N is the main nitrogen-containing product formed upon O₂ pulsing over the catalyst having been treated by ¹⁵NH₃–¹⁴NO–O₂ mixture at 723 K. The latter result strongly supports the conclusion that adsorbed ¹⁵NH₃- and ¹⁴NO-containing species are decomposed by O₂ yielding gas-phase nitrogen. Since there is a correlation between the composition of gas-phase products and the presence of adsorbed NH₂NO species we suggest that these species are intermediates in the NO reduction by NH₃. Participation of adsorbed HNO, as alternative intermediate, in the formation of N₂O and N₂ seems to be doubtful, since no indication of such adsorbates was observed in FTIR spectra during switch from NO/O₂ to H₂/Ar mixture, although direct formation of these species could be expected. Moreover, recombination of two HNO species predicts dominant formation of nitrogen and nitrous oxide molecules containing only one type of nitrogen atoms. However, ¹⁴N¹⁵N and ¹⁴N¹⁵NO were mainly formed during experiments with ¹⁵NH₃–¹⁴NO–O₂ and ¹⁵NH₃–¹⁴NO–O₂–H₂ mixtures over reduced catalyst [10]. Therefore, it is assumed that surface NH₂NO species are the major intermediates participating in the formation of N₂ and N₂O over the catalyst studied. The importance of NH_x–NO surface complexes in N₂ and N₂O formation have tentatively mentioned for low-temperature [28] and high-temperature NH₃–NO–O₂ interactions [29] over Pt-based catalysts.

Based on the isotopic distribution of reaction products shown in Fig. 3, it can be concluded that the decomposition of NH₂NO species is not the only reaction pathway leading to nitrogen and nitrous oxide. The formation of ¹⁴N₂O, formally originated from two ¹⁴NO feed molecules can be attributed to the recombination of two adsorbed NO species as reported for silver catalysts supported on Al₂O₃ [30]. However, this reaction pathway is less important in comparison to the decomposition of NH₂NO species.

Similarly, it can be expected that recombination of nitrogen atoms originating from dissociated NO species and NH₃ molecules, which passed through the whole stripping sequence (NH₂–NH–N), also contribute to the total nitrogen formation. However, the present study evidenced that in the presence of hydrogen other reaction pathways play a significant role. As it was concluded from the analysis of the shapes of the transient responses of N₂O and N₂ obtained during studies of ¹⁵NH₃–¹⁴NO–O₂–H₂ interactions (Fig. 5), in addition to the transformation of surface NH₂NO species to N₂, N₂ originates via N₂O decomposition over reduced Ag

particles. This experimental observation agrees well with previous suggestions of Burch et al. [31]. These authors studied the influence of H_2 on N_2O decomposition over a Pt/SiO_2 catalyst in the temperature range from 473 to 773 K. They explained the boosting effect of H_2 on N_2O decomposition by (i) an H-assisted N_2O dissociation mechanism and (ii) by the removal of “hot” oxygen species formed from N_2O through adsorbed hydrogen species. The latter process leads to the regeneration of reduced metallic sites active for N_2O decomposition. However, it should be noted that in NO reduction by ammonia, oxygen species originating from N_2O decomposition could participate in ammonia activation. Probably, hydrogen interacts with oxygen species yielding OH groups, which are more effective for NH_3 activation as adsorbed oxygen atoms at least on Pt and Rh catalysts [32,33].

Thus, the mechanistic effects of H_2 and O_2 on product formation in NH_3 -SCR over $2Ag/Al_2O_3$ can be summarized as follows. H_2 is required for the reduction of AgO_x at low temperatures (above 373 K) yielding reduced Ag species. The reduced Ag species catalyze generation of active oxygen species from O_2 and decomposition of primarily formed N_2O yielding gas-phase N_2 and surface oxygen species. The formed oxygen species participate in ammonia dehydrogenation yielding reactive NH_x fragments. The latter accelerate NO conversion to N_2 and N_2O via thermal or O_2 -assisted decomposition of surface NH_2NO species.

4. Conclusions

The mechanistic information obtained in the present study together with previously published results allowed to develop an improved mechanistic scheme of NO reduction with NH_3 to N_2 and N_2O in the presence of O_2 and H_2 . The results presented in this paper highlight the importance of reduced Ag species for performance of $2Ag/Al_2O_3$ in NH_3 -NO interactions. In situ UV/vis spectroscopy and HRTEM enabled to detect the reduction of AgO_x to metallic Ag starting at 373 K in a hydrogen-containing flow. The reduced Ag species decompose NO to N_2 and N_2O as well as N_2O to N_2 . However, the main reaction pathway leading to N_2 and N_2O is direct or oxygen-induced decomposition of surface NH_2NO species. These surface species are formed from NO and adsorbed NH_2 fragments, which originate from ammonia activa-

tion by adsorbed oxygen species resulting mainly from O_2 dissociation over reduced Ag species.

References

- [1] S. Satokawa, *Chem. Lett.* 29 (2000) 294.
- [2] S. Satokawa, J. Shibata, K.-I. Shimizu, A. Satsuma, T. Hattori, *Appl. Catal. B* 42 (2003) 179.
- [3] J. Shibata, K.-I. Shimizu, Y. Takada, A. Shichi, H. Yoshida, S. Satokawa, A. Satsuma, T. Hattori, *J. Catal.* 227 (2004) 367.
- [4] S. Satokawa, J. Shibata, K.-I. Shimizu, A. Satsuma, T. Hattori, T. Kojima, *Chem. Eng. Sci.* 62 (2007) 5335.
- [5] P. Sazama, L. Capek, H. Drobna, Z. Sobalik, J. Dedecek, K. Arve, B. Wichterlova, *J. Catal.* 232 (2005) 302.
- [6] K.-I. Shimizu, A. Satsuma, *J. Phys. Chem.* 111 (2007) 2259.
- [7] R. Brosius, K. Arve, M.H. Groothaert, J.A. Martens, *J. Catal.* 231 (2005) 344.
- [8] J. Shibata, Y. Takada, A. Shichi, S. Satokawa, A. Satsuma, T. Hattori, *J. Catal.* 222 (2004) 368.
- [9] M. Richter, U. Bentrup, R. Eckelt, M. Schneider, M.-M. Pohl, R. Fricke, *Appl. Catal. B* 51 (2004) 261.
- [10] E.V. Kondratenko, V.A. Kondratenko, M. Richter, R. Fricke, *J. Catal.* 239 (2006) 23.
- [11] B. Wichterlova, P. Sazama, J.P. Breen, R. Burch, C.J. Hill, L. Capek, Z. Sobalik, *J. Catal.* 235 (2005) 195.
- [12] N. Bion, J. Saussey, M. Haneda, M. Daturi, *J. Catal.* 217 (2003) 47.
- [13] M. Richter, R. Fricke, R. Eckelt, *Catal. Lett.* 94 (2004) 115.
- [14] J.T. Gleaves, G.S. Yablonsky, P. Phanawadee, Y. Schuurman, *Appl. Catal. A* 160 (1997) 55.
- [15] M. Richter, A. Abramova, U. Bentrup, R. Fricke, *J. Appl. Spectrosc.* 71 (2004) 368.
- [16] K.-I. Shimizu, M. Tsuzuki, K. Kato, S. Yokota, K. Okumura, A. Satsuma, *J. Phys. Chem. C* 111 (2007) 950.
- [17] J.P. Breen, R. Burch, C. Hardacre, C.J. Hill, *J. Phys. Chem. B* 109 (2005) 4805.
- [18] U. Bentrup, M. Richter, R. Fricke, *Appl. Catal. B* 55 (2005) 213.
- [19] G. Ramis, L. Yi, G. Busca, M. Turco, E. Kotur, R.J. Willey, *J. Catal.* 157 (1995) 523.
- [20] D.M. Thornburg, R.J. Madix, *Surf. Sci.* 220 (1989) 268.
- [21] C.T. Campbell, *Surf. Sci.* 157 (1985) 43.
- [22] M. Dean, A. McKee, M. Bowker, *Surf. Sci.* 211/212 (1989) 1061.
- [23] X. Bao, M. Muhler, T. Schedel-Niedrig, R. Schlögl, *Phys. Rev. B* 54 (1996) 2249.
- [24] A. Nagy, G. Mestl, T. Rühle, G. Weinberg, R. Schlögl, *J. Catal.* 179 (1998) 548.
- [25] D.Y. Zemlyanov, A. Nagy, R. Schlögl, *Appl. Surf. Sci.* 133 (1998) 171.
- [26] D. Zemlyanov, R. Schlögl, *Surf. Sci.* 470 (2000) 20.
- [27] X. Bao, U. Wild, M. Muhler, B. Pettinger, R. Schlögl, G. Ertl, *Surf. Sci.* 425 (1999) 224.
- [28] K. Otto, M. Shelef, J.T. Kummer, *J. Phys. Chem.* 74 (1970) 2690.
- [29] J. Pérez-Ramírez, E.V. Kondratenko, V.A. Kondratenko, M. Baerns, *J. Catal.* 229 (2005) 303.
- [30] J. Muslehiddinoglu, M.A. Vannice, *J. Catal.* 217 (2003) 442.
- [31] R. Burch, S.T. Daniells, J.P. Breen, P. Hu, *Catal. Lett.* 94 (2004) 103.
- [32] M. Baerns, R. Imbihl, V.A. Kondratenko, R. Kraehnert, W.K. Offermans, R.A. van Santen, A. Scheibe, *J. Catal.* 232 (2005) 226.
- [33] C. Popa, R.A. van Santen, A.P.J. Jansen, *J. Phys. Chem.* 111 (2007) 9839.